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SUPERACID SYSTEMS

R. J. GILLESPIE AND T. E. PEEL

*Department of Chemistry, McMaster University, Hamilton,
Ontario, Canada*

I. INTRODUCTION

IN recent years a considerable amount of fascinating new chemistry has been carried out in several highly acidic systems. This is exemplified by the preparation of stable solutions of aliphatic carbonium ions (Olah *et al.*, 1965), the formation of a variety of new inorganic cations, e.g., the I_2^+ and Se_4^{2+} cations (Gillespie, 1968), and the protonation of some unusual very weak bases such as carbonic acid to give $C(OH)_3^+$ (Olah and White, 1968). There has, however, been rather little fundamental information available on these systems and in particular on one of their most important and fundamental properties, namely their acidity. In this review we discuss the properties of systems which have acidities comparable to, or greater than, that of 100% H_2SO_4.

We may define the acidity of a medium as its tendency to donate a proton to a base. In dilute aqueous solutions acidity is measured precisely and quantitatively by the pH but in concentrated aqueous solutions or in non-aqueous systems the concept of pH is not applicable and no alternative precise and quantitative measure of acidity is generally

1

2   R. J. GILLESPIE AND T. E. PEEL

available. The most useful measure of the acidity of such a medium has proved to be the Hammett acidity function H_0 which may be defined by the equation (1)

$$H_0 = pK_{BH^+} - \log\frac{[BH^+]}{[B]} \qquad (1)$$

where pK_{BH^+} is the acid dissociation constant of the conjugate acid of a base B and $[BH^+]/[B]$ is the ionization ratio which has generally been measured spectrophotometrically. By commencing with a base, of known pK_{BH^+} whose ionization ratio could be measured in dilute aqueous sulphuric acid, and by using a set of successively weaker bases whose ionization ranges overlapped each other, Hammett and Deyrup (1932) were able to obtain H_0 values over the whole composition range for the system H_2O—H_2SO_4. The establishment of an acidity scale in this manner implies the assumption that the activity coefficient ratio $(f_C f_{BH^+})/(f_{CH^+} f_B)$ for two successive bases B and C has the value of unity. This approximation is likely to be more valid if all the bases used are of the same structural type. This was not the case for some of the bases used by Hammett and Deyrup, and recently their early data have been revised and improved by use of an extended and more closely related set of bases consisting only of primary anilines (Jorgenson and Hartter, 1963; and Johnson et al., 1969). The latest H_0 values for the H_2O—H_2SO_4 system are given in Table 1. Unfortunately other types of bases, e.g.,

TABLE 1

H_0 Values for H_2O—H_2SO_4 System at 25°C (Johnson et al., 1969)

Wt% H_2SO_4	H_0	Wt% H_2SO_4	H_0	Wt% H_2SO_4	H_0
2	0·53	36	−2·12	70	−5·82
4	0·20	38	−2·27	72	−6·13
6	−0·02	40	−2·42	74	−6·47
8	−0·20	42	−2·60	76	−6·81
10	−0·35	44	−2·77	78	−7·13
12	−0·50	46	−2·95	80	−7·46
14	−0·65	48	−3·12	82	−7·80
16	−0·78	50	−3·30	84	−8·13
18	−0·92	52	−3·48	86	−8·42
20	−1·06	54	−3·68	88	−8·71
22	−1·20	56	−3·90	90	−9·01
24	−1·34	58	−4·13	92	−9·34
26	−1·47	60	−4·37	94	−9·66
28	−1·60	62	−4·62	96	−9·98
30	−1·73	64	−4·91	98	−10·43
32	−1·85	66	−5·20		
34	−1·99	68	−5·52		

amides, do not always give the same acidity function values and indeed a number of other acidity function scales have been proposed for such bases. We do not intend to discuss the relative merits of these scales here; we only wish to emphasize that, although the H_0 values cannot be regarded as having any absolute significance, they are nevertheless extremely useful as they give at least a semi-quantitative measure of the relative acidities of different highly acidic media.

H_0 values for various H_2O—HX systems are given in Fig. 1. The data for these systems have been reviewed by Paul and Long (1957). The relative acidities of the concentrated solutions of these acids are, in general, qualitatively the same as the relative strengths of the acids in dilute aqueous solution, although HF, which is rather weak in dilute
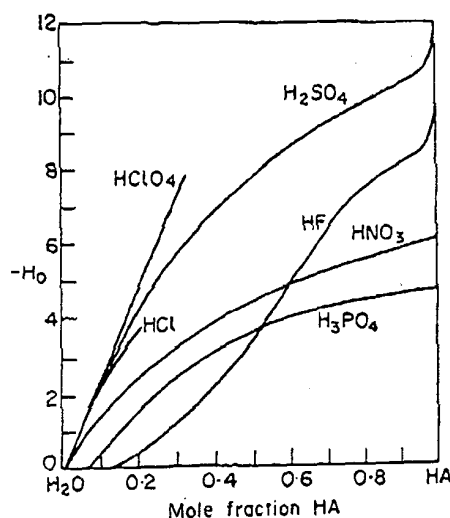
Fig. 1. Mole fraction HA.

aqueous solution, approaches the acidity of 100% H_2SO_4 in very concentrated solutions. Perchloric acid gives the highest acidities at low concentrations but for obvious reasons more concentrated solutions have not been studied.

In dilute aqueous acid systems the acidic species is H_3O^+, and the acidity is given by the H_3O^+ concentration or the pH. In sufficiently dilute solution the H_3O^+ ion is hydrated by at least three water molecules, i.e., $H_3O(H_2O)_3^+$ or $H^+(H_2O)_4$, but as the concentration of the acid HX is increased the number of water molecules available to hydrate the H_3O^+ decreases and the extent of hydration of H_3O^+ eventually decreases accordingly. As the extent of hydration of H_3O^+ decreases the hydrated complex becomes smaller, its positive charge therefore becomes more concentrated, and its acidity is therefore expected to increase. Consequently the acidity of an HX—H_2O system increases more rapidly than

4   R. J. GILLESPIE AND T. E. PEEL

the H_3O^+ concentration. At still higher HX concentrations there is not enough water to ionize all the acid and molecular HX is then present in the system. As this is a stronger proton donor than H_3O^+ the acidity of the system increases further and this continues up to 100% HX.

II. H_2SO_4 SYSTEMS

A. *100% H_2SO_4*

The most acidic system investigated over the whole composition range H_2O—HX is the sulphuric acid system. Following the work of Hammett and Deyrup (1933) and Treffers and Hammett (1937) and the earlier pioneer work of Hantzsch (1907–1909), concentrated sulphuric acid and 100% H_2SO_4 have become the most extensively studied and well-understood acidic media and thus have received rather wide application in both preparative and mechanistic studies (Gillespie and Robinson, 1965; Gillespie, 1968).

Some of the properties of 100% H_2SO_4 are summarized in Table 2. Although it has been the best known and most widely used of the super-

TABLE 2

Some Physical Constants of Sulphuric Acid

Freezing point	10·371°C
Boiling point	290–317°C
Density (25°C)	1·8269 g cm⁻³
Viscosity (25°C)	24·54 centipoise
Dielectric constant (25°C)	100
Specific conductance (25°C)	$1·0439 \times 10^{-2}$ ohm⁻¹ cm⁻¹

acid media some of its properties as a solvent and reaction medium are less than ideal. In particular its high viscosity is inconvenient in preparative reactions as solid products are difficult to filter from the acid solvent although adhering sulphuric acid solvent can often be conveniently removed by washing with liquid sulphur dioxide. Another disadvantage of 100% H_2SO_4 is its relatively high freezing point of 10·37° which precludes the study of solutions at low temperatures. Thus for the study of protonations at temperatures at which proton exchange is relatively slow, fluorosulphuric acid, with a freezing point of $-89°$, has proved much superior.

Hammett and Deyrup (1932) gave H_0 values up to 100% H_2SO_4 but their values at the highest concentrations were based on the use of 2,4,6-trinitroaniline as an indicator. The basicity of this indicator is

really too great to enable it to be used with any accuracy beyond approximately 99·5% H_2SO_4. As no significantly weaker primary aniline base can probably be obtained it is necessary to turn to another type of indicator in order to extend the acidity scale to 100% H_2SO_4 and to media with still higher acidities. The indicators which have been used for this purpose are a set of aromatic nitrocompounds which, when suitably substituted, have basicities that enable a rather wide range of acidities to be measured. Almost all the H_0 values quoted in this review are based on the use of these nitro compound indicators. The ionization ratio data for the most basic nitrocompound indicator used, p-nitrotoluene, appears to overlap the data for the least basic aniline, 2,4,6-trinitroaniline, in a satisfactory manner. Thus the plots of ionization ratios against solvent composition for the two indicators are parallel and lead to a constant value for the pK_{BH^+} of p-nitrotoluene. The pK_{BH^+} values along with the extinction coefficients of the protonated (ϵ_{BH^+}) and unprotonated (ϵ_B) forms of a number of weak nitrocompound bases are shown in Table 3. The measured ionization ratios for these

TABLE 3

pK_{BH^+} Values of Aromatic Nitrocompound Indicators

| Indicator	pK_{BH^+}	ϵ_{BH^+}	ϵ_B
2,4,6-Trinitroaniline	−10·10	200	8,500
p-Nitrotoluene	−11·85	19,200	2,100
m-Nitrotoluene	−11·99	16,100	1,200
Nitrobenzene	−12·14	15,150	900
p-Nitrofluorobenzene	−12·44	16,500	600
p-Nitrochlorobenzene	−12·70	24,350	400
m-Nitrochlorobenzene	−13·16	14,380	440
2,4-Dinitrotoluene	−13·76	13,900	1,700
2,4-Dinitrofluorobenzene	−14·52	12,100	920
2,4,6-Trinitrotoluene	−15·60	10,600	960
1,3,5-Trinitrobenzene	−16·04	10,700	800
(2,4-Dinitrofluorobenzene)H$^+$	−17·57*	20,000*	1,000

* Estimated.

bases over a wide range of acidity indicate that they form a satisfactory consistent set of indicators.

The new indicators have been used to obtain a value of H_0 for 100% H_2SO_4 which is −11·93 (Gillespie et al., 1971). Although the acidity function scale based on the use of the nitrocompounds may not form a completely satisfactory extension of the scale based upon the anilines, the use of these indicators does give at least a semi-quantitative picture of the acidity of various superacid systems. Moreover the H_0 values for

6   R. J. GILLESPIE AND T. E. PEEL

superacid media obtained from the nitrocompound indicators are in
satisfactory qualitative agreement with such other methods as are
available for determining the acidity of these media.

Although 100% H_2SO_4, according to its H_0 value, is approximately
10^{13} times as acidic as a 0·1N aqueous H_2SO_4 solution, it is by no means
the most acidic medium that can be obtained. One method of obtaining
a more acidic medium, at least in principle, is to dissolve in H_2SO_4 a
substance HA that is capable of protonating H_2SO_4, i.e., an acid of the
sulphuric acid solvent system,

$$HA + H_2SO_4 \rightleftharpoons H_3SO_4^+ + A^- \tag{2}$$
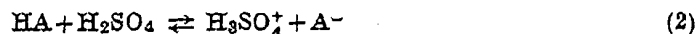
Some of these systems plus other equally acidic systems are described in
this review. We may somewhat arbitrarily classify 100% H_2SO_4 and
other non-aqueous systems containing considerably more acidic species
than the hydrated proton as superacid systems as their acidities are of a
different order of magnitude from that encountered in the more familiar
aqueous systems.

B. H_2SO_4—SO_3

One of the earliest of the superacid systems to be recognized was
oleum, i.e., sulphuric acid containing an excess of sulphur trioxide; this
has often been used when a very powerful acid catalyst was required.
A number of fundamental studies have established that it contains a
series of polysulphuric acids $H_2S_nO_{3n+1}$ which increase in chain length
with increasing sulphur trioxide concentration (Gillespie and Robinson,
1962). The main component of dilute oleums is disulphuric acid,
$H_2S_2O_7$, and it has been shown that this ionizes as a moderately strong
acid of the H_2SO_4 solvent system (Bass et al., 1960).

$$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-, \quad K_a = 0·014 \tag{3}$$
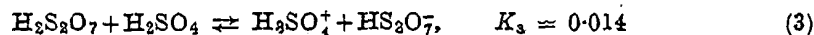
There is therefore a substantial increase in the concentration of the
$H_3SO_4^+$ ion in such a medium and hence a corresponding increase in
acidity. On increasing the concentration of SO_3 in an oleum, the amount
of $H_2S_3O_{10}$ and still higher polysulphuric acids increases significantly.
At the composition $H_2S_2O_7$, there are extensive amounts of $H_2S_3O_{10}$
and higher polysulphuric acids and of course a corresponding amount of
H_2SO_4 (Gillespie and Malhotra, 1967). The extent of ionization of a
number of weakly basic nitrocompounds has been determined by cryo-
scopic and conductimetric measurements in oleum having the compo-
sition $H_2S_2O_7$ (Gillespie and Malhotra, 1968). The ionization constants
determined by these methods are compared with those found for the

SUPERACID SYSTEMS   7

same bases in H_2SO_4 in Table 4. It may be seen that these nitrocompounds are much more extensively ionized in $H_2S_2O_7$ than in H_2SO_4 and it may therefore be concluded that $H_2S_2O_7$ is a considerably more acidic medium than H_2SO_4.

TABLE 4

Comparison of K_B Values for Some Weak Bases in H_2SO_4, HSO_3F and $H_2S_2O_7$ (Gillespie and Malhotra, 1968)

	$10^2 K_B$		
	H_2SO_4	HSO_3F	$H_2S_2O_7$
p-Nitrotoluene	9·5		Fully ionized
m-Nitrotoluene	2.3	Fully ionized	
Dimethylsulphone	1.5	8	Fully ionized
Nitrobenzene	1.0	Fully ionized	Fully ionized
p-Nitrochlorobenzene	0·4	76	Fully ionized
m-Nitrochlorobenzene		7.9	65
Nitromethane	0·25	2·7	Fully ionized
2,4-Dinitrotoluene	0·05	1·4	Fully ionized
m-Dinitrobenzene	0·03	0·26	26
2,4-Dinitrochlorobenzene	Non-electrolyte	0·16	10
2,4-Dinitrofluorobenzene	Non-electrolyte	0·16	10

Values of the Hammett acidity function for these systems were first given by Lewis and Bigeleisen (1943) who proposed that for fuming sulphuric acid the acidity function could be determined from the vapour pressure of SO_3 above the solution. However, as pointed out by Paul and Long (1957), there is no particular reason to expect the acidity to be related to the SO_3 pressure. The acidity function measurements of Brand (1950) and Brand et al. (1952) confirmed, by the use of aromatic nitrocompound indicators, that the acidity does indeed increase with increasing concentration of SO_3 but Brand's H_0 values do not appear to be related to the vapour pressure of SO_3.

The H_0 values determined by Brand were based on an earlier value of H_0 for 100% H_2SO_4 which has now been superseded. Also he was, in several cases, unable to obtain the nitrocompound indicators in the fully ionized form, which led to errors in the determination of the ionization ratios. Consequently his values have been revised and the latest values are listed in Table 5 (Gillespie et al., 1971) and are also shown in Fig. 2. Although an increase in acid strength would be expected with increasing chain length in the polysulphuric acids, this would be most marked

8   R. J. GILLESPIE AND T. E. PEEL

TABLE 5

H_0 Values for the Systems H_2O—H_2SO_4 (near 100% H_2SO_4), H_2SO_4—SO_3, H_2SO_4—$HB(HSO_4)_4$, H_2SO_4—HSO_3Cl, H_2SO_4—HSO_3F, H_2SO_4—$H_2S_2O_7$

| | | H_2O—H_2SO_4 | | | |
Mole% H_2O	Wt% H_2SO_4	H_0	Mole% H_2O	Wt% H_2SO_4	H_0
10·00	98·0	−10·44	4·20	99·2	−10·93
9·07	98·2	−10·50	3·18	99·4	−11·05
8·13	98·4	−10·56	2·14	99·6	−11·15
7·17	98·6	−10·62	1·08	99·8	−11·40
6·20	98·8	−10·71	0·54	99·9	−11·64
5·21	99·0	−10·84	0·0	100·0	−11·93

| | | H_2SO_4—SO_3 | | | |
Mole% SO_3	H_0	Mole% SO_3	H_0	Mole% SO_3	H_0
1·00	−12·24	25·00	−13·58	55·00	−14·69
2·00	−12·42	30·00	−13·76	60·00	−14·74
5·00	−12·73	35·00	−13·94	65·00	−14·84
10·00	−13·03	40·00	−14·11	70·00	−14·92
15·00	−13·23	45·00	−14·28	75·00	−14·96
20·00	−13·41	50·00	−14·44		

| | H_2SO_4—$HB(HSO_4)_4$ | | | |
Mole% $HB(HSO_4)_4$	H_0	Mole% $HB(HSO_4)_4$	H_0
1·00	−12·35	10·00	−13·23
2·00	−12·60	15·00	−13·39
4·00	−12·87	20·00	−13·49
6·00	−13·03	25·00	−13·56
8·00	−13·15	30·00	−13·62

| Mole% HA | H_0 | | |
	$H_2S_2O_7$	HSO_3F	HSO_3Cl
1·00	−12·23	−12·02	−11·98
2·00	−12·41	−12·09	−12·08
5·00	−12·71	−12·25	−12·15
10·00	−12·98	−12·41	−12·28
20·00	−13·28	−12·60	−12·47
30·00	−13·52	−12·75	−12·61
40·00	−13·71	−12·86	−12·72
50·00	−13·88	−13·02	−12·84
60·00	−14·03	−13·14	−12·94
70·00	−14·17	−13·28	−13·06
80·00	−14·26	−13·47	−13·19
90·00	−14·36	−13·73	−13·38
95·00	−14·40	−13·95	−13·54
97·50	−14·42	−14·14	−13·66
99·00	−14·43	−14·21	−13·74
100·00	−14·44	−15·07	−13·80

between the first few members of the series and probably becomes negligible from $H_2S_4O_{13}$ onwards. It seems reasonable to suppose that in very concentrated oleums, as the concentration of protons decreases, the acidity must again fall off to low values. However, no data are available for this region of the system.

C. H_2SO_4—$HB(HSO_4)_4$

The only known strong acid of the sulphuric acid system is tetra(hydrogensulphato)boric acid, $HB(HSO_4)_4$, which may be obtained in solution in sulphuric acid by dissolving boric acid in oleum in the amount required by equation (4) (Flowers *et al.*, 1956).

$$H_3BO_3 + 3H_2S_2O_7 \rightarrow HB(HSO_4)_4 + 2H_2SO_4 \qquad (4)$$
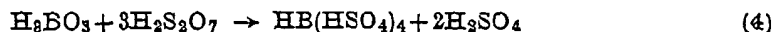
This acid is a strong acid that is extensively although not quite completely ionized

$$HB(HSO_4)_4 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + B(HSO_4)_4^- \qquad (5)$$
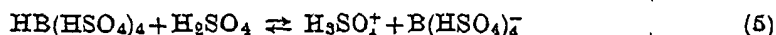
Table 5 and Fig. 2 show that H_0 for $HB(HSO_4)_4$ solutions increases more rapidly than for solutions of either HSO_3F or $H_2S_2O_7$, which is consistent with this acid being a stronger acid than either HSO_3F or $H_2S_2O_7$ (Gillespie *et al.*, 1971). The acidity that can be obtained in solutions of $HB(HSO_4)_4$ is however limited by the separation of insoluble complex polysulphatoboric acids from more concentrated solutions.

III. HSO_3F AND HSO_3Cl SYSTEMS

A. H_2SO_4—HSO_3F

Cryoscopic and conductimetric measurements on dilute solutions of HSO_3F in H_2SO_4 have shown that HSO_3F behaves as a rather weak acid of the H_2SO_4 solvent system (Barr *et al.*, 1961) ionizing to a small extent according to equation (6):

$$HSO_3F + H_2SO_4 \rightleftharpoons H_3SO_4^+ + SO_3F^-, \qquad K_a = 3 \times 10^{-3} \qquad (6)$$
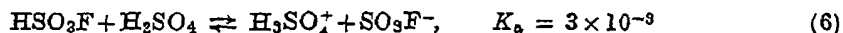
Hence one may reasonably conclude that addition of fluorosulphuric acid to sulphuric acid increases the acidity of the medium and this increase might be expected to continue throughout the H_2SO_4—HSO_3F system up to the composition 100% HSO_3F. Cryoscopic and conductimetric studies (Barr *et al.*, 1964; Gillespie *et al.*, 1966) in 100% HSO_3F as solvent have confirmed that this is the case as a series of nitrocompound weak bases are more extensively ionized in HSO_3F than in H_2SO_4 (Table 4). Values of H_0 for the H_2SO_4—HSO_3F system have been obtained (Gillespie *et al.*, 1971) using the bases nitrobenzene, *p*-chloronitrobenzene, *m*-nitrobenzene and 2,4-dinitrotoluene and these are summarized in Table

10   R. J. GILLESPIE AND T. E. PEEL

5 and Fig. 2. They show that addition of HSO_3F to H_2SO_4 produces a
fairly rapid increase in H_0 initially, although this is less than that
produced by $H_2S_2O_7$, which is consistent with the fact that $H_2S_2O_7$ is a
stronger acid. This is followed by a slower steady increase in acidity and
another very rapid increase in the region of 100% HSO_3F. The rapid
increase in the vicinity of 100% HSO_3F is presumably to be associated
with the self-ionization of HSO_3F.

$$2HSO_3F \rightleftharpoons H_2SO_3F^+ + SO_3F^- \tag{7}$$
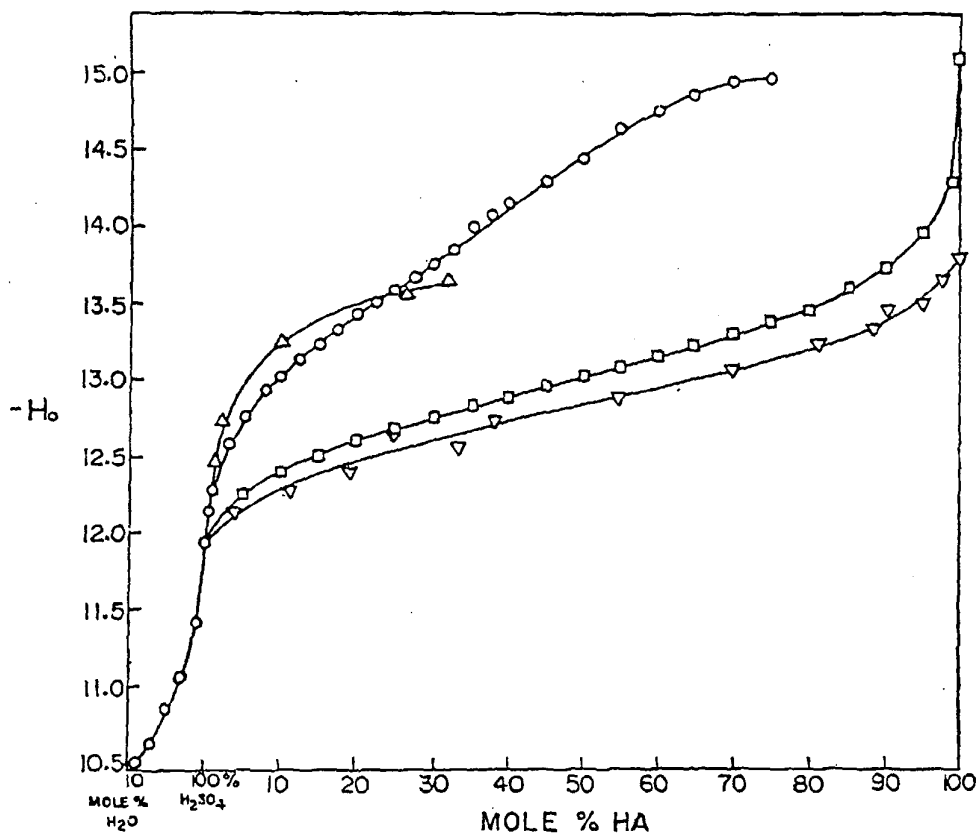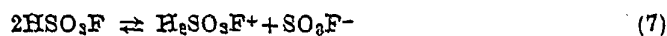
Fig. 2. Acidity function values for the systems H_2SO_4—$HB(HSO_4)_4$ ($\triangle$), H_2SO_4—SO_3 (o), H_2SO_4—HSO_3F ($\square$), H_2SO_4—HSO_3Cl ($\triangledown$).

As the concentration of the very weakly basic H_2SO_4 decreases to a very
low value and the concentration of SO_3F^- decreases accordingly, so the
concentration of the highly acidic $H_2SO_3F^+$ ion increases rapidly up
to the value that it has in 100% HSO_3F. Some of the properties of
fluorosulphuric acid are summarized in Table 6. Fluorosulphuric acid
has a boiling point of 163·7°C and it is therefore easily removed by
distillation from a reaction mixture; it is also readily purified by distil-

TABLE 6

Physical Properties of Fluorosulphuric Acid

Freezing point	$-88 \cdot 98°C$
Boiling point	$162 \cdot 7°C$
Density (25°C)	$1 \cdot 726$ g cm^{-3}
Viscosity (25°C)	$1 \cdot 56$ centipoise
Specific conductance (25°C)	$1 \cdot 085 \times 10^{-4}$ ohm^{-1} cm^{-1}

lation although the last traces of sulphur trioxide are difficult to remove completely. When free from HF, fluorosulphuric acid does not attack glass and is thus easily and conveniently handled in conventional glass apparatus. Although the acidity of HSO_3F is not much greater than that of $H_2S_2O_7$, it is generally a much more useful highly acidic medium (Gillespie, 1968) and there are two main reasons for this. Firstly, its freezing point is low ($-89°C$). This has proved to be particularly important in the study of the protonation of weak bases by proton n.m.r., as many proton exchange reactions with the solvent are very slow at this temperature. Secondly, it is a considerably poorer sulphonating agent towards organic compounds than is $H_2S_2O_7$, particularly at low temperatures, and, in general, stable solutions of many more substances can be obtained in HSO_3F than in $H_2S_2O_7$.

It is clear that by increasing the concentration of $H_2SO_3F^+$ by the addition of an acid of the HSO_3F solvent system, which ionizes according to equation (8),

$$HA + HSO_3F \rightleftharpoons H_2SO_3F^+ + A^- \qquad (8)$$
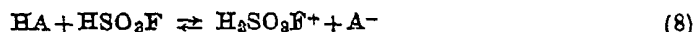
the acidity of the system could be further increased. No simple acids are known as all the common protonic acids are non-electrolytes or bases in solution in HSO_3F. However some Lewis acids act as fluorosulphate ion acceptors and hence increase the $H_2SO_3F^+$ concentration.

B. HSO_3F—SO_3

Sulphur trioxide causes a marked increase in the acidity of H_2SO_4 because of its ionization as a moderately strong acid of the sulphuric acid solvent system. Freezing point measurements (Gillespie et al., 1966) show, however, that SO_3 behaves as a non-electrolyte in solution in HSO_3F, and this is confirmed by the observation that SO_3 causes a negligible increase in the conductivity. On the other hand, the Raman spectra of solutions of SO_3 in HSO_3F contain new lines that are not due to either SO_3 or HSO_3F and it has been shown by Gillespie and Robinson (1962) that they can be attributed to the acid HS_2O_6F (1). It must be concluded that, in contrast to the behaviour of $H_2S_2O_7$ in H_2SO_4,

12   R. J. GILLESPIE AND T. E. PEEL

(1)   (2)
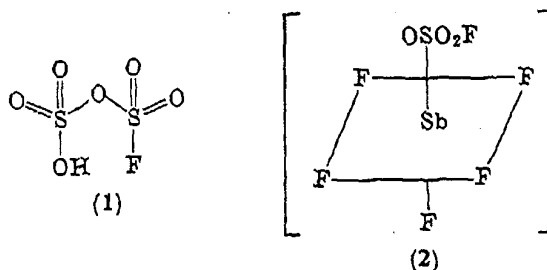
the acid HS_2O_6F is not a sufficiently strong acid of the HSO_3F solvent system to ionize to an appreciable extent. This is confirmed by the very small increase in $-H_0$ produced by SO_3 in HSO_3F (Fig. 4).

C. $HSO_3F—MF_5$ and $HSO_3F—MF_5—SO_3$

Conductivity and cryoscopic measurements (Thompson *et al.*, 1965; Gillespie *et al.*, 1969) on solutions of several pentafluorides in HSO_3F have shown that PF_5 and NbF_5 are non-electrolytes, AsF_5 and BiF_5 are very slightly ionized and SbF_5 is a moderately strong acid

$$SbF_5 + 2HSO_3F \rightleftharpoons H_2SO_3F^+ + SbF_5(SO_3F)^- \qquad (9)$$
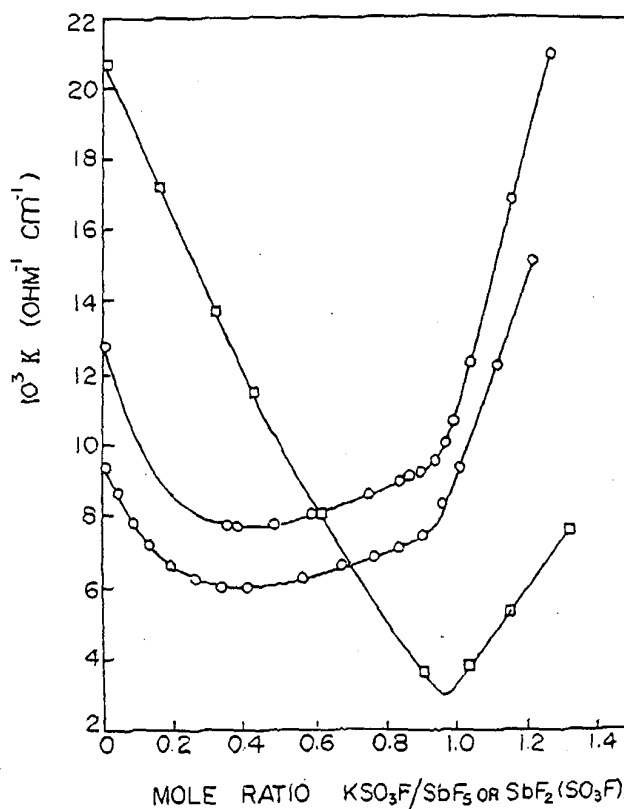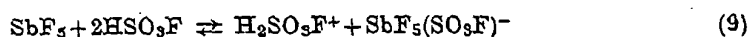
FIG. 3. Titration of SbF_5 with KSO_3F (O) and of SbF_5 $3SO_3$ with KSO_3F (□).

The ions $SbF_5SO_3F^-$ and $AsF_5SO_3F^-$ have the octahedral structure (2). The fact that SbF_5 behaves as an acid rather than as a base has been confirmed by conductimetric titrations with a fluorosulphate (Fig. 3) (Thompson *et al.*, 1965; Gillespie *et al.*, 1969). The concentrations of $H_2SO_3F^+$ and SO_3F^- are easily followed in such titrations because these two ions have considerably greater mobilities than other ions (Barr *et al.*, 1964). Thus the conductivity decreases on addition of SO_3F^- to an SbF_5 solution because the highly conducting $H_2SO_3F^+$ ion is replaced by the considerably less mobile K^+ ion. Since $H[SbF_5(SO_3F)]$ is not a strong acid of the HSO_3F solvent system, the conductivity passes through a minimum before the end point corresponding to the mole ratio $KSO_3F/H[SbF_5(SO_3F)] = 1$. A slow increase is followed by a sharp break at the 1/1 end point, as the excess SO_3F^- ion produces a marked increase in the conductivity.

$$H[SbF_5(SO_3F)] + KSO_3F \rightarrow K[SbF_6(SO_3F)] + HSO_3F \qquad (10)$$
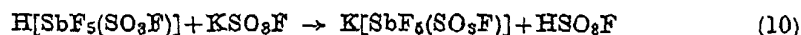
Values for the acidity function H_0 of the HSO_3F—SbF_5 and HSO_3F—AsF_5 systems up to the mole ratio 1/0.25 are given in Table 7 and Fig. 4 (Gillespie and Peel, 1971). We see that there is a very marked increase in the acidity on the addition of SbF_5 to HSO_3F which corresponds to the

TABLE 7

HSO_3F-MF_5, H_0 Values

Mole% MF5	H_0		Mole% MF5	H_0	
	AsF5	SbF5		AsF5	SbF5
0·00	−15·07	−15·07	2·50	−16·37	−18·19
0·05	−15·22	−15·98	3·00	−16·42	−81·26
0·10	−15·36	−16·55	3·50	−16·48	−18·31
0·15	−15·48	−16·89	4·00	−16·52	−18·35
0·20	−15·56	−17·04	6·00		−18·43
0·30	−15·70	−17·26	8·00		−18·57
0·40	−15·80	−17·37	10·00		−18·50
0·50	−15·88	−17·45	12·00		−18·53
0·75	−16·03	−17·66	14·00		−18·56
1·00	−16·12	−17·80	16·00		−18·59
1·50	−16·24	−17·98	18·00		−18·62
2·00	−16·31	−18·10	20·00		−18·65

very rapid increase in the concentration of the very highly acidic $H_2SO_3F^+$ ion. AsF_5 gives a much smaller increase in acidity consistent with its behaviour as a very weak acid. At a concentration of SbF_5 of approximately 5 mole% the acidity function curve flattens out and higher concentrations of SbF_5 produce only a very small further increase in the acidity. This is consistent with the conclusion from cryoscopic,

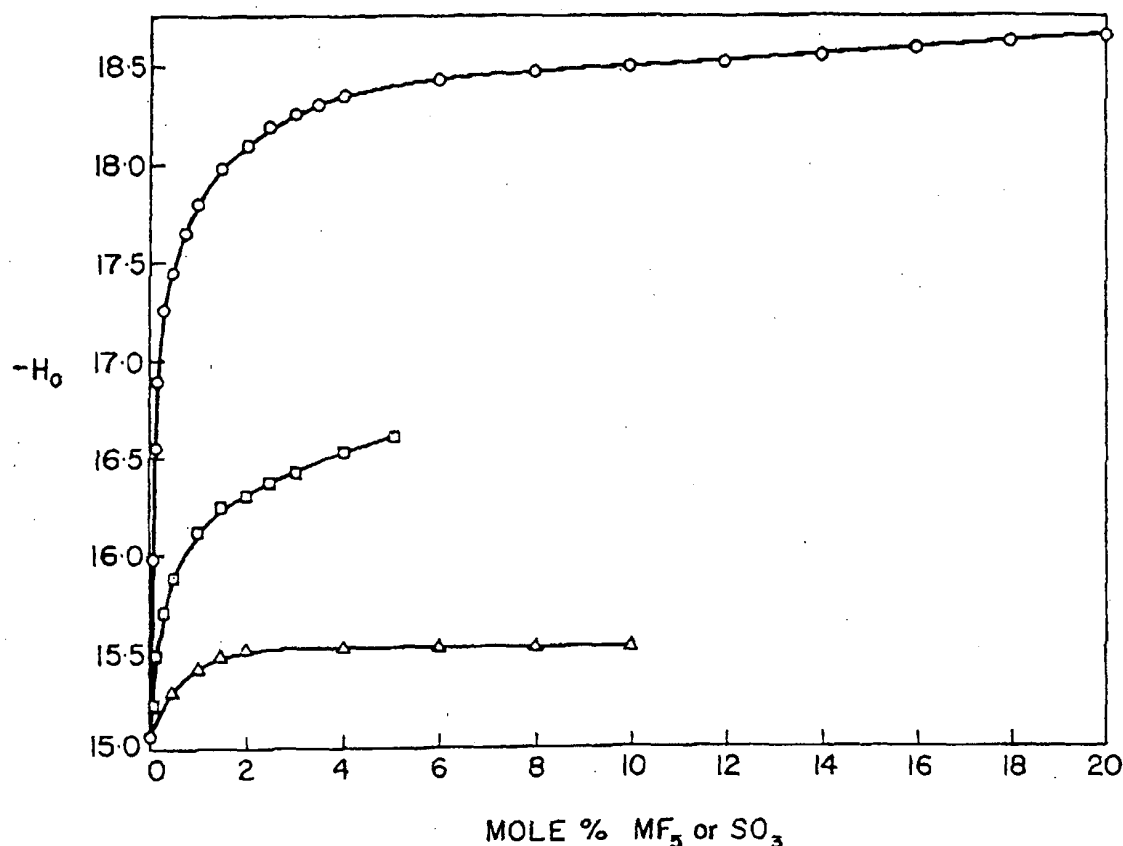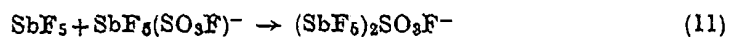14   R. J. GILLESPIE AND T. E. PEEL

MOLE % MF$_5$ or SO$_3$

FIG. 4. Acidity function values for the systems.
HSO$_3$F – SbF$_5$ (o), HSO$_3$F – AoF$_5$ (□), HSO$_3$F – SO$_3$ (△).

conductimetric, and n.m.r. measurements (Thompson *et al.*, 1965) that
with increasing concentration much of the SbF$_5$ forms a dimeric anion
according to equation (11).

$$SbF_5 + SbF_5(SO_3F)^- \rightarrow (SbF_5)_2SO_3F^- \tag{11}$$

Although H[(SbF$_5$)$_2$SO$_3$F] is probably a somewhat stronger acid than
H[SbF$_5$(SO$_3$F)] there is no direct increase in the concentration of
H$_2$SO$_3$F$^+$. The anion (SbF$_5$)$_2$SO$_3$F$^-$ has the structure (3) involving a
bridging fluorosulphate group.

(3)
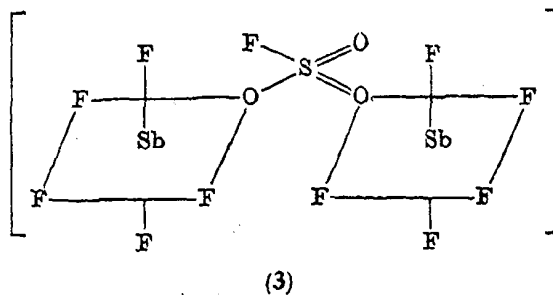
When sulphur trioxide is added to a solution of SbF_5 in HSO_3F there is a marked increase in the conductivity which continues until approximately three moles of SO_3 have been added per mole of SbF_5 originally present (Thompson et $al.$, 1965). This increase in conductivity must be due to an increase in the concentration of the highly conducting $H_2SO_3F^+$ ion arising from the formation of a stronger acid than $H[SbF_5(SO_3F)]$ in the system. From the results of these measurements, combined with cryoscopic and ^{19}F n.m.r. studies, it has been concluded that a series of acids $H[SbF_4(SO_3F)_2]$, $H[SbF_3(HSO_3F)_3]$, and $H(SbF_2(SO_3F)_4]$ are formed which increase in acidic strength through the series. Dimeric ions such as (4) are also formed at high concentrations. The acid $H[SbF_2(SO_3F)_4]$ appears to be a fully ionized strong acid of the HSO_3F solvent system. This can be shown for example by a conductimetric titration of a solution of the acid with a base such as KSO_3F. The conductivity decreases on addition of KSO_3F and passes through a minimum at the mole ratio $KSO_3F/H[SbF_2(SO_3F)_4] = 1$ as expected for a strong acid (Fig. 3). No H_0 measurements have yet been made on these systems; however it is expected that the acidity will be somewhat greater than that found in the HSO_3F—SbF_5 system.
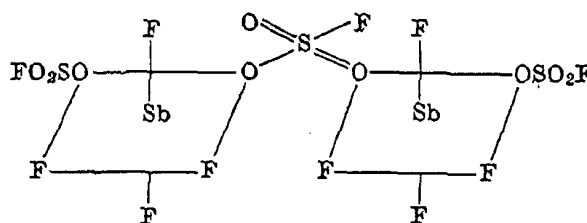
(4)

Sulphur trioxide similarly causes an increase in the conductivity of solutions of AsF_5 in HSO_3F (Gillespie et $al.$, 1969). Presumably acids such as $H[AsF_2(SO_3F)]_4$ are formed but they appear to be somewhat weaker than the corresponding antimony acids, just as AsF_5 forms a weaker acid in HSO_3F than SbF_5.

D. H_2SO_4—HSO_3Cl

This system was originally studied by Palm (1956) but his results were based on the older value of the H_0 of H_2SO_4 which has now been revised. New measurements have also been made on this system (Gillespie et $al.$, 1971) and these, together with a recalculation of Palm's data, lead to the values listed in Table 5. The acidity of this system is very similar to that of the HSO_3F system with the acidity of HSO_3Cl being close to that of HSO_3F.

16   R. J. GILLESPIE AND T. E. PEEL

IV. HF Systems

A. H_2O—HF

Hydrogen fluoride is a weak acid in dilute solution in water but H_0 measurements (Bell *et al.*, 1956) show that in more concentrated solutions the acidity rises rapidly so that 100% HF has an H_0 value only slightly less than that of 100% H_2SO_4. Confirmation of this comes from cryoscopic measurements which show that the weak bases water, acetonitrile and *p*-nitrotoluene are somewhat less ionized in 100% HF than in 100% H_2SO_4 (Gillespie and Humphreys, 1970).

The exact value of H_0 for pure 100% HF is uncertain as it appears to depend strongly on the presence of small amounts of impurities which are very difficult to remove: the most important of these is water which exhibits weak basic behaviour. Thus the measured values of $-H_0$ increase from 9·7 to 11·0 with decreasing impurity concentration, as indicated by the electrical conductivity (Hyman and Katz, 1965). The value of $-11·0$ was obtained with an acid that had a conductivity of 3×10^{-5} ohm^{-1} cm^{-1} at 0°. Presumably, if the last traces of water and other impurities could be removed from HF, the value of $-H_0$ would be greater than 11·0, perhaps as high as 11·5. A few measurements have been made on solutions of sodium fluoride, which causes a marked decrease in $-H_0$, and on a 0·02M solution of NbF_5, which had $H_0 \simeq -12·5$ (Hyman *et al.*, 1961).

TABLE 8

Physical Properties of Anhydrous Hydrogen Fluoride

|	
Freezing point	$-89·37°C$
Boiling point	19·51°C
Density (0°C)	1·002 g cm^{-3}
Dielectric constant (0°C)	84
Specific conductance (0°C)	$\sim 1 \times 10^{-6}$ ohm^{-1} cm^{-1}

Some of the physical properties of HF are summarized in Table 8. Hydrogen fluoride is a good solvent for a wide variety of organic and inorganic solutes; it has a high dielectric constant, a low viscosity and its low boiling point is an advantage in its use as a preparative solvent. Its major disadvantage as a solvent is of course the fact that it attacks glass. However with the advent of fluorinated plastic materials such as Kel-F and Teflon the use of apparatus constructed from these materials, in conjunction with the use of metal vacuum lines equipped with needle valves containing Teflon and Kel-F, has made the handling and use of anydrous HF a relatively simple matter.

B. *Lewis Acids in HF*

It has been shown from cryoscopic (Dean *et al.*, 1970) and conductimetric (Gillespie and Moss, 1966) measurements that SbF_5 is a strong acid in HF ionizing in dilute solutions according to equation (13).

$$SbF_5 + HF \rightarrow H_2F^+ + SbF_6^- \qquad (13)$$
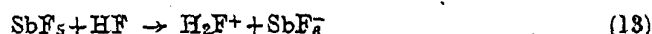
At higher concentration of SbF_5 the anions $Sb_2F_{11}^-$ (5), $Sb_3F_{16}^-$ (6), etc. are formed with increasing concentrations of SbF_5. Presumably, therefore, there is very little increase in acidity when the formation of these ions predominates over the formation of SbF_6^-.
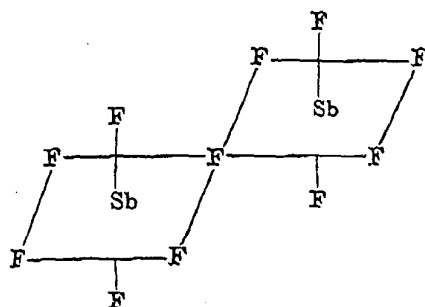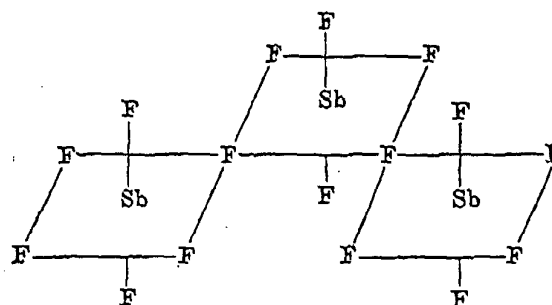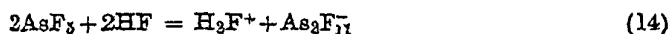

(5)   (6)

Solutions of arsenic pentafluoride have conductivities and freezing point depressions (Dean *et al.*, 1970) that are only approximately one-half those of SbF_5 at the same concentration and it has been shown that even in dilute solutions there is essentially complete formation of the $As_2F_{11}^-$ ion according to equation (14).

$$2AsF_5 + 2HF = H_2F^+ + As_2F_{11}^- \qquad (14)$$

These solutions are thus less acidic than those of antimony pentafluoride because the H_2F^+ concentration is lower. PF_5 appears to behave as a non-electrolyte and it must be concluded that it is too weak a fluoride ion acceptor to enhance the acid properties of hydrogen fluoride (Dean *et al.*, 1970). The strong proton acid HSO_3F exhibits no appreciable acid properties in HF (Gillespie and Humphreys, 1970).

Some other pentafluorides have been placed in order of their acidity on the basis of their effectiveness in increasing the amount of *m*- and *p*-xylenes extracted from *n*-heptane solution into an excess of hydrogen fluoride (McCauley *et al.*, 1956). It was found that $TaF_5 > NbF_5 > TiF_4 > PF_5 > PbF_2$ but all these fluorides appear to be weaker acids than SbF_5 and AsF_5. The low solubility of BF_3 and the low electrical conductivity of its solutions also suggest that it is a weaker acid than SbF_5 and AsF_5 (Kilpatrick and Luborsky, 1964).
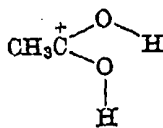
V. APPLICATIONS

A. *Protonation Studies*

Considerable use has been made of superacid systems, particularly the HSO_3F—SbF_5 system, for the preparation and identification of the conjugate acids of some very weak bases. The ternary system HSO_3F—SbF_5—SO_2 has also often been used for such studies. Although SO_2 is completely miscible with HSO_3F—SbF_5 mixtures, it is not protonated to any measurable extent and it does not appear to cause any appreciable reduction of the very high acidity of HSO_3F—SbF_5. Sulphur dioxide also considerably reduces the rather high viscosity of SbF_5—HSO_3F solutions and this gives rise to sharper and better resolved n.m.r. spectra.

One of the earliest applications of the HSO_3F—SbF_5 medium was the first observation of the proton magnetic resonance spectra of the conjugate acids of acetic, propionic and benzoic acids at temperatures of $-70°$ and lower (Birchall and Gillespie, 1965). At these temperatures proton exchange between the solvent and the conjugate acid is sufficiently slow that the spectra for acetic and propionic acids showed, in addition to the expected peaks for the alkyl groups, two equally intense signals at very low field due to protons on oxygen. It was concluded that these arise from structure (7). More recent work (Brookhart *et al.*, 1967) using an HSO_3F—SbF_5—SO_2 solvent has shown that there are other weak signals in the spectrum which may be attributed to the other isomeric form of the conjugate acid (8) in which both protons on oxygen are equivalent. Isomer (8) is present to the extent of only 3% in the case of acetic acid but the corresponding forms of protonated formic acid are present in approximately equal amounts in HSO_3F—SbF_5—SO_2 at $-60°$.

The spectrum of the conjugate acid of acetone was observed for the first time in HSO_3F—SbF_5, the $=OH^+$ proton giving a signal at -14.5 ppm downfield from tetramethylsilane (Birchall and Gillespie, 1965). Protonated methyl ethyl ketone shows two resonances for the proton on oxygen at -14.3 and -13.9 ppm in SbF_5—HSO_3F—SO_2 below $-20°C$ due to 81% of isomer (9) and 19% of isomer (10) (Olah *et al.*, 1967).

(7)   (8)

The structures (9), (10), (11), (12) are drawn as protonated aldehyde/ketone species.
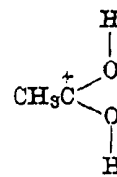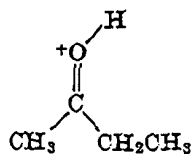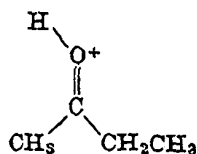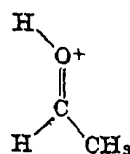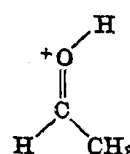
(9)   (10)   (11)   (12)

The n.m.r. spectra of the conjugate acids of aldehydes can similarly be observed in the same medium at $-60°$. The spectrum of acetaldehyde, for example, clearly indicates the presence of both the *cis* and *trans* isomers (11) and (12) of its conjugate acid.

Sodium and potassium carbonates were found to dissolve in 1:1 HSO_3F—SbF_5 at $-78°$ without the evolution of carbon dioxide (Olah and White, 1968). A single low field peak in the proton n.m.r. spectrum was assigned to $C(OH)_3^+$, protonated carbonic acid. On warming the solution the peak disappeared and was replaced by another peak characteristic of water in this medium and carbon dioxide was evolved. The assignment of the low field peak to $C(OH)_3^+$ was confirmed by observation of the C^{13} spectrum which proved to be the expected quartet due to coupling with the three equivalent protons.

Many solutes containing more than one basic group undergo multiple protonation in superacid systems. An interesting example is the biologically important biotin which is triprotonated to give (13) (Olah and White, 1968).
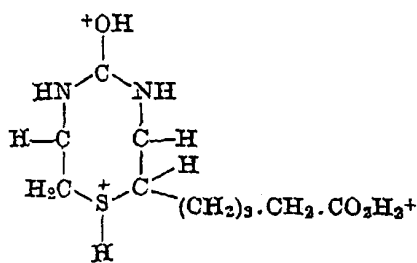
(13)

B. *New Cations*

1. *Introduction*

Highly acidic systems in general have very low basicities although the acidity and basicity of a given medium are not directly related. Indeed the fact that superacid solvents such as HSO_3F undergo a significant autoprotolysis, in which solvent molecules act as both acid and base, shows that the basic properties of these solvents are not completely negligible. Nevertheless, the basicities of these highly acidic solvents are sufficiently low that many highly electrophilic species, particularly

20   R. J. GILLESPIE AND T. E. PEEL

cations, can be obtained as stable species in these solvents although they do not exist in more basic media such as water. Although there is not necessarily any direct relation between the basicity of a medium towards a proton and towards other cations, the highly acidic systems described have in fact been found to have very low basicities towards many cations as well as towards the proton.

One of the early applications of a superacid medium was the preparation and identification of the nitronium ion NO_2^+ from nitric acid dissolved in 100% H_2SO_4.

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + H_3O^+ + 2HSO_4^- \qquad (15)$$
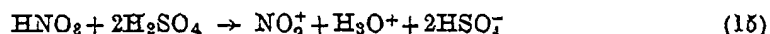
This reaction may be considered to proceed by protonation to give $H_2NO_3^+$ followed by dissociation to H_2O and NO_2^+. This is driven to completion by the protonation of H_2O by the acid medium, thus shifting the equilibrium to the right. A more basic solvent, such as water, attacks the highly electrophilic NO_2^+ cation to re-form nitric acid. Since the nitronium ion is the active reagent in aromatic nitration it was postulated that other electrophilic aromatic substitution reactions proceeded by similar mechanisms involving cation intermediates such as I^+, Br^+ and SO_3H^+. Although no evidence has been found for these particular cations, the search for them has in fact led to the discovery of other new cations, such as I_2^+, which can conveniently be obtained as stable species in solution in a superacid solvent.
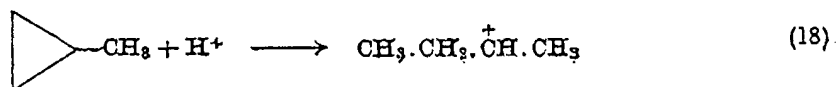
2. Carbonium ions

A very early application of a superacid solvent was the use of 100% H_2SO_4 for the preparation of stable solutions of carbonium ions, such as the triphenylcarbonium ion (Hantzsch, 1908c) $(C_6H_5)_3C^+$, e.g.,

$$(C_6H_5)_3COH + 2H_2SO_4 \rightarrow (C_6H_5)_3C^+ + H_3O^+ + 2HSO_4^-. \qquad (16)$$
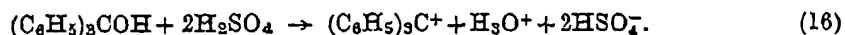
More recently a large variety of different carbonium ions have been prepared in various highly acidic media. For example t-butanol is completely converted to the trimethylcarbonium ion in HSO_3F—SbF_5—SO_2 at $-60°$ (Olah et al., 1967). Stable solutions of the same carbonium ion can be obtained by protonation of 2-methylpropene in HF—SbF_5 at low temperature (Brouwer et al., 1968).

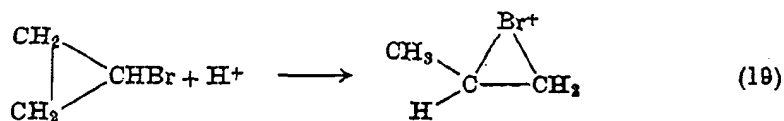$$(CH_3)_2C{=}CH_2 + H^+ \rightarrow (CH_3)_3C^+ \qquad (17)$$
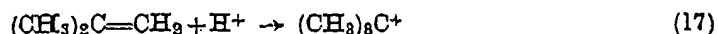
In the same medium methylcyclopropane is protonated to give the methylethylcarbonium ion

$$\triangleright\!\!-CH_3 + H^+ \longrightarrow CH_3.CH_2.\overset{+}{C}H.CH_3 \qquad (18)$$

On protonation, in HSO_3F—SbF_5—SO_2, cyclopropyl bromide undergoes an interesting rearrangement to give a bromonium ion (Olah and Bollinger, 1968).

$$CH_2 \diagdown \diagdown CHBr + H^+ \longrightarrow CH_3 \diagdown C \diagup Br^+ \diagdown CH_2 \qquad (19)$$

Many aromatic hydrocarbons can be protonated in various superacid media. For example m-xylene is protonated in HF—SbF_5 at $-45°$ to give the conjugate acid (14) (Mackor et al., 1965), and fluorobenzene in
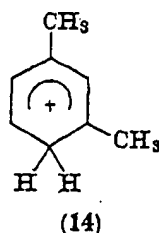
HSO_2F—SbF_5 at low temperature gives the fluorobenzenonium ion (15).

Oxocarbonium ions (acyl ions) are readily generated in superacid media. For example, Deno et al. (1964) found that the n.m.r. chemical shift of the methyl protons in a solution of acetic acid in oleum underwent a marked change at about 20% SO_3 which they attributed to the dehydration of the conjugate acid $CH_3.CO_2H_2^+$ to give the methyl oxocarbonium ion CH_3CO^+. The same reaction also occurs in HSO_3F—SbF_5—SO_2 when the temperature is increased from $-40°$ to $-10°$ (Olah and White, 1967).

## 3. Halogen cations

There has always been considerable interest in the halogen cations and it has often been postulated that the simple ions I^+, Br^+, and Cl^+ are the reactive intermediates in aromatic halogenation reactions. No convincing evidence has ever been obtained for these cations; however, the search for them has led to the discovery of the I_2^+ cation and a number of other related halogen cations (Gillespie and Morton, 1970) which are stable in superacid media. The I_2^+ cation can be conveniently prepared by the oxidation of I_2 with $S_2O_6F_2$ in solution in HSO_3F.

$$2I_2 + S_2O_6F_2 \rightarrow 2I_2^+ + 2SO_3F^- \qquad (20)$$
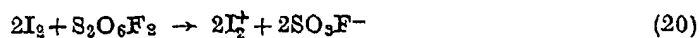
A stable, intensely blue, solution of this cation can also be obtained by oxidizing iodine with 65% oleum. In a more basic medium such as

22   R. J. GILLESPIE AND T. E. PEEL

H_2SO_4 the I_2^+ cation is almost completely disproportionated to the more stable $+1/3$ and $+3$ oxidation states.

$$8I_2^+ + 3HSO_4^- \rightleftharpoons I(HSO_4)_3 + 5I_3^+ \tag{21}$$
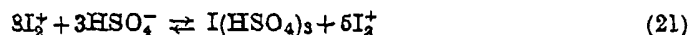
The more electrophilic Br_2^+ cation can only be obtained in the extremely weakly basic superacid HSO_3F—SbF_5—SO_3 and does not appear to exist in any measurable concentration in HSO_3F because of disproportionation according to an equation similar to that for iodine above. The presumably still more electrophilic Cl_2^+ cation has not yet been observed in solution and it would appear to need a medium even less basic than HSO_3F—SbF_5—SO_3. In addition to I_2^+ and Br_2^+, the cations I_5^+, I_3^+, Br_3^+ and Cl_3^+ have also been obtained in superacid media. In accordance with the expectation that the X_3^+ cations would be less electrophilic than the X_2^+ cations, due to the greater dispersal of their positive charge, they can be obtained in more basic media than the X_2^+ cations. Thus I_3^+ is stable in H_2SO_4 but I_2^+ is not. Br_3^+ is stable in HSO_3F while Br_2^+ is only stable in the superacid HSO_3F—SbF_5—SO_3.

4. *Cations of other non-metallic elements*

It has been known for a very long time that the elements sulphur, selenium and tellurium give coloured solutions when they dissolve in a number of highly acid media. For example sulphur gives red, blue and pale yellow solutions in oleum depending on the concentration of the oleum. Investigations on the nature of these solutions have been made since the early 1800's but it has only very recently been shown that these colours correspond to the formation of the S_{16}^{2+}, S_8^{2+} and S_4^{2+} cations respectively (Gillespie and Passmore, 1970). They are formed by oxidation of the element by sulphur trioxide according to equations such as (22).

$$4S + 6H_2S_2O_7 \rightarrow S_4^{2+} + 2HS_3O_{10}^- + 5H_2SO_4 + SO_2 \tag{22}$$
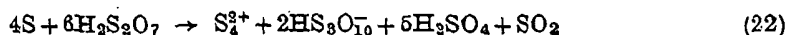
Selenium can be oxidized even by 100% H_2SO_4 to a dark green solution and by oleum, to an orange solution which have been shown to contain the Se_8^{2+} and Se_4^{2+} cations respectively. These sulphur and selenium cations can also be prepared in other very weakly basic media. For example, solutions of these cations in fluorosulphuric acid can be conveniently obtained by oxidizing the element with $S_2O_6F_2$.

$$4Se + S_2O_6F_2 = Se_4^{2+} + 2SO_3F^- \tag{23}$$
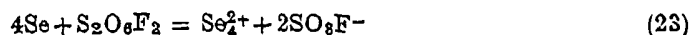
The fact that tellurium gives a red solution in concentrated sulphuric acid was reported in the first paper published on tellurium by its discoverer Klaproth in 1798 but the origin of this colour remained a mystery until very recently when it was shown to arise from the Te_4^{2+} cation. Tellurium differs from sulphur and selenium however in that the two other

cations that have been discovered are Te_4^{4+} and Te_6^{2+}. These are not at present known for the other elements. Like the halogen cations the sulphur, selenium and tellurium cations are highly electrophilic and they undergo disproportionation in media with any appreciable basic properties although as would be anticipated the ease of disproportionation increases in the series tellurium < selenium < sulphur. For example none of the sulphur cations can be obtained in 100% H_2SO_4 and they all disproportionated in this medium according to equations such as (24)

$$2S_4^{2+} + 4H_2SO_4 = SO_2 + 7S + 4H^+ + 2H_2S_2O_7 \tag{24}$$
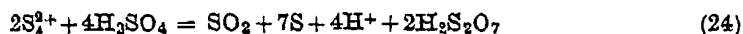
whereas the tellurium cation Te_4^{2+} is quite stable even in 98% H_2SO_4.

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2

24 R. J. GILLESPIE AND T. E. PEEL

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